Co-ordinative Interactions in Chelated Complexes of Silicon. Part 5.[1] Chirality of Five-co-ordinate Silicon Compounds: Crystal and Molecular Structures † of 1-(Chlorodimethylsilyl)- and 1-(Dichloromethylsilyl)-1,2,3,4-tetrahydro-1,10-phenanthroline

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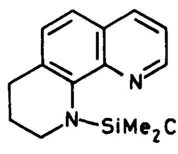
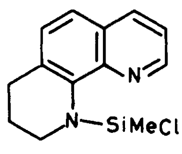
The crystal and molecular structures of 1-(chlorodimethylsilyl)-1,2,3,4-tetrahydro-1,10-phenanthroline, $(C_{12}H_{11}N_2)SiMe_2Cl$ (1), and 1-(dichloromethylsilyl)-1,2,3,4-tetrahydro-1,10-phenanthroline, $(C_{12}H_{11}N_2)SiMeCl_2$ (2), have been determined from diffractometer data. Both compounds crystallize isostructurally with orthorhombic symmetry (space group *Pnam*). For (1): a = 1 857.3(6), b = 1 028.6(7), c = 723.3(5) pm, Z = 4; 7 258 observed reflections, R' = 0.053. For (2): a = 1 853.4(4), b = 1 024.2(4), c = 720.3(1) pm, Z = 4; 3 658 observed reflections, R' = 0.033. The central Si has a trigonal-bipyramidal five-co-ordination. The molecular arrangement of ligands in the first co-ordination sphere of Si is achiral in (1) whereas Si occupies a centre of chirality in (2) and both enantiomeric forms are found in the same crystal. The co-ordinative Si $\cdots$ N bonds [202.8(7) pm in (1) and 202.7(4) pm in (2)] are extended 14.6% [for (1)] and 16.6% [for (2)] in comparison with the other intramolecular Si–N single bond [177.0(6) pm in (1) and 173.9(3) pm in (2)]. The topological arrangement around silicon is discussed with respect to stereochemistry of intermediates along the S_N2 pathway.

Chirality is often observed in the stereochemistry of carbon, especially in naturally occurring organic compounds. It results either from the chirality of the whole molecular framework (*e.g.* DNA, twistane, hexahelicene) or, as in most cases, from the presence of an asymmetrically substituted tetrahedral centre (*e.g.* amino acids). However, left- and right-handed molecules also occur with atoms which have co-ordination numbers greater than four. In these cases asymmetric molecular centres are constituted not only when all ligands are chemically different, but also for an arrangement of identical groups which excludes intramolecular mirror planes (symmetry C_n or D_n).

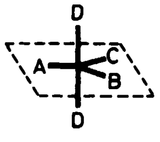
In the present study, two five-co-ordinate silicon complexes (1) and (2) are described with four chemically different substituents (A,B,C,D) on the five sites of a trigonal bipyramid. Under these conditions two achiral arrangements (I,II) and one chiral arrangement (III) around silicon have to be considered. In order to investigate which of the possible topological geometries are formed by reaction, the crystal structures of the two chemically similar derivatives (1) and (2) were determined.



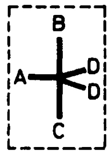
(1)



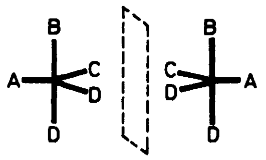
(2)



I



II



III

Experimental

Crystal Structures of (1) *and* (2).—The compounds (1) and (2) were prepared by substitution reactions of 1,2,3,4-tetrahydro-1-lithio-1,10-phenanthroline with the corresponding chlorosilane $SiMe_2Cl_2$ or $SiMeCl_3$, respectively.[2] Crystals were obtained by sublimation under vacuum (*ca.* 0.01 Torr) with a temperature gradient of 105/108 °C for (1) or 118/120 °C for (2). Because of the extreme sensitivity to moisture, the crystal preparation was carried out in a glove box carefully dried under vacuum over P_2O_5 before use. The specimens for *X*-ray investigation were sealed in glass capillaries. Both compounds crystallize in the same orthorhombic space group (*Pna*2₁ or *Pnam*, Z = 4) with slightly different lattice constants.

Crystal data for (1). $C_{14}H_{17}ClN_2Si$, M = 276.85, a = 1 857.3(6), b = 1 028.6(7), c = 723.3(5) pm, U = 1 381.9 × 10^6 pm^3.

Crystal data for (2). $C_{13}H_{14}Cl_2N_2Si$, M = 297.27, a = 1 853.4(4), b = 1 024.2(4), c = 720.3(1) pm, U = 1 367.3 × 10^6 pm^3.

Data for (1) and (2) were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Cu-K_α [for (1)] or Mo-K_α radiation [for (2)] in the ω-scan mode up to $(\sin\theta)/\lambda$ = 0.562 and 0.807 Å^{-1}, resulting in 7 258 and 3 658 observations for (1) and (2) respectively. Three standard reflections monitored at regular intervals did not show any significant variation in intensity. After application of background correction (SDP system[3]) and averaging symmetry-

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† *Supplementary data available* (No. SUP 56025, 67 pp.): thermal parameters, structure factors, full bond distances and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix.

Non-S.I. unit employed: Torr = 133.3 Pa.

Table 1. Atomic co-ordinates for $(C_{12}H_{11}N_2)SiMe_2Cl$ (1), with standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cl(1)	0.840 0(2)	0.493 7(2)	0.7500	C(9)	0.834 0(5)	1.006(1)	0.7500
C(15)	0. 807 3(3)	0.728 5(6)	0.976 2(7)	C(12)	0.978 0(4)	1.056 3(7)	0.7500
Si	0·857 0(1)	0.712 1(2)	0.7500	C(14)	1.064 8(4)	0.8304(7)	0.7500
N(1)	0.952 2(3)	0.703 2(7)	0.7500	H(9)	0.779(3)	0.984(6)	0.750
N(10)	0.878 2(3)	0.905 5(6)	0.7500	H(8)	0.826(3)	1.197(6)	0.750
C(13)	0.991 1(4)	0.818 9(8)	0.7500	H(7)	0.948(3)	1.271(5)	0.750
C(11)	0.949 9(4)	0.929 9(8)	0.7500	H(6)	1.073(3)	1.162(4)	0.750
C(2) *	0.994 7(7)	0.587(1)	0.704(3)	H(5)	1.145(3)	0.963(5)	0.750
C(3) *	1.064 2(7)	0.588(1)	0.794(8)	H(41) *	1.118(4)	0.659(8)	0.62(1)
C(4)	1.109 9(5)	0.708(1)	0.7500	H(42) *	1.146(4)	0.720(7)	0.842(9)
C(5)	1.093 5(4)	0.957(1)	0.7500	H(31) *	1.094(3)	0.485(5)	0.78(2)
C(6)	1.053 2(5)	1.068 7(9)	0.7500	H(32) *	1.046(5)	0.572(8)	0.94(1)
C(7)	0.930 7(4)	1.160 9(7)	0.7500	H(21) *	0.987(5)	0.562(7)	0.56(1)
C(8)	0.858 9(6)	1.135 4(9)	0.7500	H(22) *	0.972(3)	0.475(5)	0.73(3)

* Population 0.5.

Table 2. Atomic co-ordinates for $(C_{12}H_{11}N_2)SiMeCl_2$ (2), with standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cl(1)	0.844 83(7)	0.494 3(1)	0.7500	C(9)	0.833 8(2)	0.999 5(5)	0.7500
Si	0.862 37(6)	0.707 4(1)	0.7500	C(12)	0.979 5(2)	1.055 5(4)	0.7500
Cl(2) *	0.807 1(3)	0.722 1(5)	0.504 6(6)	C(14)	1.068 4(2)	0.833 3(4)	0.7500
C(15) *	0.807 9(8)	0.750(1)	0.968(2)	H(9)	0.779(2)	0.984(3)	0.750
N(1)	0.956 1(2)	0.699 2(3)	0.7500	H(8)	0.826 (2)	1.197(3)	0.750
N(10)	0.881 2(2)	0.902 3(3)	0.7500	H(7)	0.948(1)	1.271(3)	0.750
C(13)	0.994 7(2)	0.816 7(4)	0.7500	H(6)	1.073(1)	1.162(2)	0.750
C(11)	0.951 2(2)	0.928 8(4)	0.7500	H(5)	1.145(1)	0.963(2)	0.750
C(2) *	1.001 8(3)	0.585 8(5)	0.700 2(9)	H(41) *	1.118(2)	0.659(4)	0.624(6)
C(3) *	1.0745(3)	0.590 7(6)	0.801(2)	H(42) *	1.146(2)	0.720(3)	0.842(5)
C(4)	1.116 9(2)	0.713 7(5)	0.7500	H(31) *	1.094(1)	0.485(3)	0.775(13)
C(5)	1.096 8(2)	0.963 6(5)	0.7500	H(32) *	1.046(2)	0.572(4)	0.937(6)
C(6)	1.053 7(2)	1.069 7(5)	0.7500	H(21) *	0.987(2)	0.562(4)	0.560(6)
C(7)	0.928 4(2)	1.157 0(4)	0.7500	H(22) *	0.972(1)	0.475(3)	0.727(14)
C(8)	0.857 5(3)	1.128 3(5)	0.7500				

* Population 0.5.

equivalent observations, 1 118 and 2 181 unique reflections, for (1) and (2) respectively, remained for structure analysis.

The structures were determined by direct methods by applying the MULTAN program.[4] Refinement with all reflections converged in the centric space group *Pnam* for (1) to a final $R = 0.099$ ($R' = 0.053$) and for (2) to $R = 0.114$ ($R' = 0.033$). In the acentric space group $Pna2_1$ no significant improvement of the agreement factors was obtained. The positional parameters of all atoms including those in the disordered arrangement at silicon and of the more saturated ring agree within 3σ in both space groups. Positional parameters and anisotropic thermal parameters of non-hydrogen atoms [except C(15), which was refined isotropically] were refined by full-matrix least-squares procedures with the programs of the *X*-RAY system.[5] Final atomic co-ordinates are given in Tables 1 and 2.

Results and Discussion

Interatomic distances and bond angles are reported in Tables 3 and 4 with the numbering scheme of Figure 1 [compound (1), equatorial plane C(15),C(15′); compound (2), equatorial plane Cl(2), C(15)].

Topology.—Both compounds are characterized by trigonal-bipyramidal co-ordinated silicon. The co-ordinated pyridine-type nitrogen N(10) occupies one of the apical positions and the nitrogen of the more saturated ring, bonded by a single

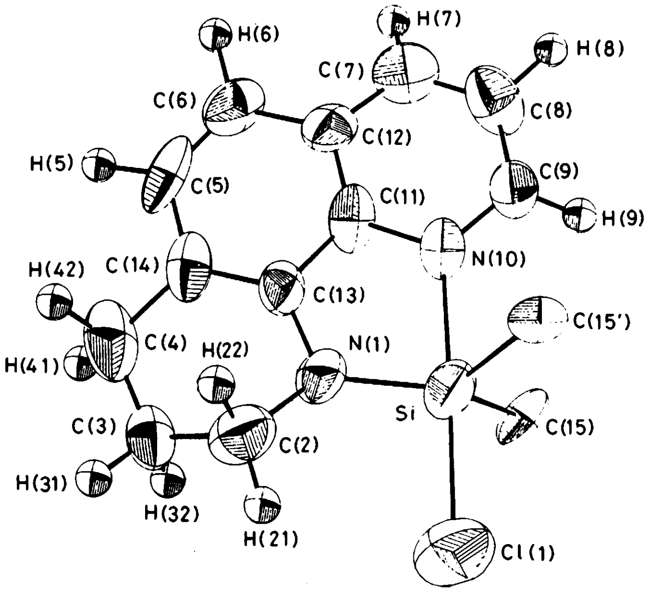

Figure 1. Molecular structure of (1); the thermal ellipsoids are the 50% probability surfaces

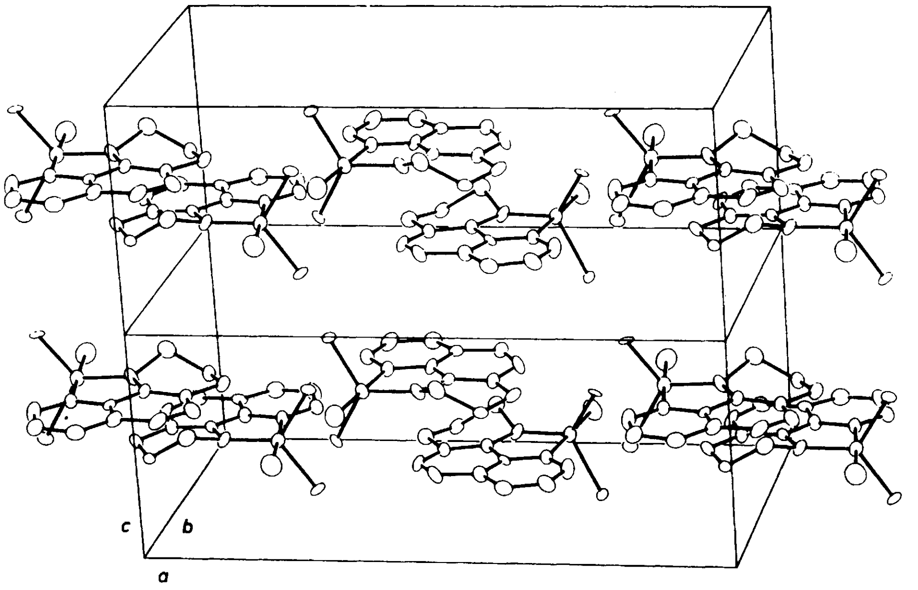

Figure 2. Molecular packing of (1) and (2) in the unit cell

bond to silicon, is located in the equatorial plane. This arrangement of the ligand skeleton excludes the first of the above mentioned stereoisomers (I). In both structures a chlorine atom is found in the axial position, opposite the co-ordinated 'pyridine' nitrogen. Structure refinement of (1) revealed two methyl carbon atoms in the remaining equatorial positions, whereas in (2) disorder between a chlorine and a methyl carbon was discovered. In the best model for the structure of (2) the two sites in the equatorial plane involved in the C/Cl disorder were split into two scattering centres occupied by half a chlorine and half a carbon atom. The two equatorial sites are related to each other by mirror symmetry (*Pnam*, see Figure 2). Refinements of both structures in the acentric space group $Pna2_1$ were performed but without any significant improvement. A possible participation of the axial chlorine atom in the disordered occupation of the two equatorial sites was checked and can be excluded. The apical position is therefore exclusively occupied by chlorine. The refined model of a crystal structure contains the averaged and superimposed information over all unit cells of the crystal. The crystallographically averaged arrangement of (2) shows four centres in the equatorial plane involved in the disordered occupancy. In agreement with the stoicheiometry of (2) a pairwise separation (C/Cl and Cl/C) leads to two geometrical isomers of $(C_{12}H_{11}N_2)SiMeCl_2$. Presumably these species are statistically distributed over the crystal. Regarding the inner co-ordination sphere around silicon, the two arrangements might be attributed to the *R* and *S* form of the molecule. A chemical disproportionation of (2) into $(C_{12}H_{11}N_2)SiMe_2Cl$ and $(C_{12}H_{11}N_2)SiCl_3$, forming a solid solution in the crystal, is rather unlikely. The ^1H n.m.r. spectra of soluted crystals of (2) show the correct integrated intensity ratio between $Si{-}CH_3$ protons and those in the ligand skeleton.[6] Due to the puckering of the more saturated heterocyclic ring, the ligand skeleton in (1) and (2) exhibits mirror symmetry for an individual molecule For this reason the two superimposed arrangements of (2) (see above) are not exactly enantiometric to each other. Only on the average over the whole crystal is mirror symmetry for the more saturated ring obtained. To check whether the disorder of C(2) and C(3) and the hydrogens bound to these carbons is an artefact of space group choice, the results in *Pnam* have to be compared to those in the acentric space group $Pna2_1$. In $Pna2_1$ no constraints like mirror symmetry of the ligand skeleton are demanded. Refinements converge to very large and prolate thermal parameters for C(2) and C(3). A split model with two conformations of the more hydrogenated ring was applied. The two conformations found in $Pna2_1$ correspond to the disordered arrangement which is obtained in *Pnam* as a result of space group symmetry.

Table 3. Interatomic distances (pm) in (1), (2), and $(C_{12}H_{11}N_2)SiCl_3$ (3)

	(1)	(2)	(3)
Si–Cl(1)	226.9(4)	220.7(2)	215.0(2)
Si–C(15)	188.6(5)	191.4(15)	—
Si–Cl(2)	—	204.9(5)	209.4(1)
Si–N(1)	177.0(6)	173.9(3)	173.7(3)
Si–N(10)	202.8(7)	202.7(4)	198.4(2)
N(1)–C(13)	139.3(10)	140.0(5)	140.1(3)
N(1)–C(2)	147.5(16)	148.3(6)	148.2(5)
N(10)–C(11)	135.6(11)	132.5(5)	134.9(4)
N(10)–C(9)	131.6(12)	132.8(6)	132.8(5)
C(13)–C(11)	137.4(12)	140.3(6)	139.7(4)
C(13)–C(14)	137.4(11)	137.7(5)	137.6(5)
C(11)–C(12)	140.1(13)	140.0(6)	140.9(3)
C(2)–C(3)	144.6(25)	153.2(10)	148.0(7)
C(3)–C(4)	153.8(18)	153.0(8)	153.0(5)
C(4)–C(14)	151.1(13)	151.9(6)	149.8(6)
C(5)–C(6)	136.8(15)	134.9(7)	135.2(6)
C(5)–C(14)	141.1(15)	143.4(6)	142.0(4)
C(6)–C(12)	140.3(15)	138.3(6)	141.5(5)
C(7)–C(8)	136.0(15)	134.7(7)	136.4(6)
C(7)–C(12)	138.9(13)	140.6(6)	140.0(5)
C(8)–C(9)	141.4(13)	139.1(7)	138.6(4)

As shown by *X*-ray diffraction, compound (1) has with respect to the inner co-ordination sphere around silicon the achiral geometry II, whereas (2) prefers the chiral arrangements III and the two enantiomeric forms are found in the same crystal.

Bond Distances and Angles.—As shown in Tables 1 and 2, the stereochemical structure of the ligand skeleton is rather similar in the two compounds (1) and (2). The stereochemistry

Table 4. Bond angles (°) in (1), (2), and (3)

	(1)	(2)	(3)
Cl(1)–Si–C(15)	91.2(2)	98.4(4)	—
Cl(1)–Si–Cl(2)	—	89.9(1)	92.41(3)
Cl(1)–Si–N(1)	95.0(2)	95.7(1)	96.24(9)
Cl(1)–Si–N(10)	176.8(2)	178.5(1)	179.44(9)
C(15)–Si–C(15′)	120.3(2)	—	—
C(15)–Si–Cl(2)	—	115.2(5)	—
Cl(2)–Si–Cl(2′)	—	—	111.88(5)
N(1)–Si–N(10)	81.8(3)	82.8(2)	84.3(1)
N(1)–Si–C(15)	119.6(2)	122.6(5)	—
N(1)–Si–Cl(2)	—	120.2(1)	123.41(3)
N(10)–Si–C(15)	90.4(2)	82.4(4)	—
N(10)–Si–Cl(2)	—	90.8(1)	87.28(6)
Si–N(1)–C(13)	118.3(5)	118.0(3)	117.1(2)
Si–N(1)–C(2)	125.3(7)	127.5(3)	128.5(2)
C(13)–N(1)–C(2)	114.7(7)	112.4(3)	114.4(3)
Si–N(10)–C(11)	111.8(5)	111.7(3)	111.1(2)
Si–N(10)–C(9)	130.2(6)	128.6(3)	129.8(2)
C(11)–N(10)–C(9)	118.0(7)	119.7(4)	119.1(2)
N(1)–C(13)–C(11)	114.9(7)	114.2(3)	113.9(3)
N(1)–C(13)–C(14)	126.2(8)	127.9(4)	127.0(3)
C(11)–C(13)–C(14)	118.9(8)	117.9(4)	119.1(2)
N(10)–C(11)–C(13)	113.2(7)	113.2(4)	113.6(2)
C(13)–C(11)–C(12)	124.4(8)	123.0(4)	123.3(3)
N(1)–C(2)–C(3)	112.0(10)	111.2(5)	114.2(3)
C(2)–C(3)–C(4)	114.0(10)	111.3(6)	113.3(4)
C(3)–C(4)–C(14)	111.4(8)	111.2(4)	108.5(4)
C(6)–C(5)–C(14)	124.6(9)	122.1(4)	124.2(2)
C(5)–C(6)–C(12)	118.0(9)	120.3(4)	119.2(3)
C(8)–C(7)–C(12)	118.1(8)	119.7(4)	120.0(3)
C(7)–C(8)–C(9)	120.2(8)	121.1(4)	120.4(4)
N(10)–C(9)–C(8)	122.3(8)	120.1(4)	121.2(3)
C(11)–C(12)–C(6)	117.0(8)	118.0(4)	116.8(3)
C(11)–C(12)–C(7)	119.0(9)	115.7(3)	116.0(3)
C(6)–C(12)–C(7)	124.0(9)	126.3(4)	127.1(3)
C(13)–C(14)–C(4)	118.8(8)	119.1(4)	119.7(3)
C(13)–C(14)–C(5)	117.1(8)	118.6(4)	117.5(3)
C(4)–C(14)–C(5)	124.1(8)	122.2(3)	122.8(3)

of (1) and (2) can be explained by regarding the five-co-ordinate silicon as a 'frozen-in' intermediate of a bimolecular substitution process at a tetrahedral centre. In both cases a strongly polarizable chlorine atom is located across from the 'attacking' nitrogen N(10) ('substrate') and can be regarded as a leaving group. Accordingly, the axial Si–Cl bonds are lengthened considerably as compared with Si–Cl distances in four-co-ordinated silicon halides (average 204 pm). The co-ordinative Si–N(10) bond is extended by 14.6% in (1) and 16.6% in (2), compared with the respective intramolecular Si–N single bonds, which display values often found for Si–N connections. The equatorial bonds to C and Cl are slightly extended in comparison to those in four-co-ordinated cases.

Together with the results for the trichlorosilyl derivative (3) of the same type of ligand,[7] a comparison of the bond lengths around silicon (Table 4) shows that the distances to the neighbouring atoms Cl(1), N(1), N(10) increase with decreasing number of chlorine atoms in the silyl group. In contrast, the equatorial Si–Cl [(3) > (2)] and the Si–C [(2) > (1)] are contracted in the series. In (1) silicon is most weakly bonded to the axial chlorine and it can be assumed that the central atom is at least shielded to nucleophilic attack. These findings explain the growing sensitivity to moisture from (3) to (2) to (1). This result is rather astonishing, because sensitivity to moisture normally increases in proportion to an increasing number of chlorine atoms in the silyl group, for statistical reasons. Furthermore, the simultaneous extension of the bond distances to the 'substrate' N(10) and the 'leaving group' Cl(1) in the series from (3) to (1) contradicts the assumption that the three structures can be associated with subsequent situations along the S_N2 reaction pathway.[8–11] Possibly the mutual influence of the exchange of the equatorial substituents (more electronegative and polarizable Cl $\longrightarrow$ electropositive CH_3) from (3) to (2) to (1) on the third equatorial ligand N(1) and the two axial ones [N(10), Cl(1)] has to be considered and corrected for a more detailed correlation of the bond increments.

The molecular packing of (1) and (2) is shown in Figure 2. As the major parts of the ligand, N(1), C(4), Si, and Cl(1) are all located on a mirror plane of *Pnam*, a layer structure perpendicular to the *c* axis is formed. The distance between the stacks amounts to half of the translation in *c* and the layers are interlocked by the equatorial substituents at silicon. The intermolecular contacts are found to be in the range of van der Waals interactions.

Acknowledgements

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